



PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF: Eric J. BERGMAN
APPLICATION NO.: 09/621,028
FILED: JULY 21, 2000
FOR: **PROCESS AND APPARATUS FOR TREATING A
WORKPIECE SUCH AS A SEMICONDUCTOR
WAFER**

EXAMINER: Z. El-Arini
ART UNIT: 1746
CONF. NO: 4066

TRANSMITTAL LETTER

Mail Stop Appeal Brief - Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Further to the Notice of Appeal filed concurrently herewith, enclosed is Applicant's Appeal Brief Under 37 CFR § 1.192, in triplicate; a check for the filing fee in the amount of \$330; and a return postcard.

Dated: June 30, 2004

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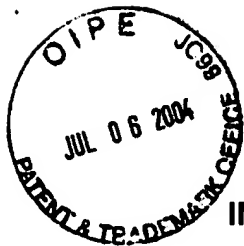
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APPEAL BRIEF UNDER 37 CFR § 1.192

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Sir:

This Appeal Brief is in response to the Final Office Action mailed April 9, 2004.

The pending claims are attached as an Appendix.

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Appeal Brief Under 37 CFR § 1.192(c)

1. Real party in interest – Semitool, Inc.
2. Related appeals and interferences – None.
3. Status of claims – Claims 1-14, 17, 19-21, 23, and 26-34 stand rejected;
Claims 15-16, 18, 22, and 24-25 have been cancelled;
Claims 1-14, 17, 19-21, 23, and 26-34 are appealed.
4. Status of amendments – No amendments have been filed subsequent to the April 9, 2004 Final Office Action.
5. Summary of Invention - The appealed claims describe methods and systems for processing or cleaning a workpiece, for example, a silicon wafer. Claims 1, 2, 26 and 27 describe cleaning methods and systems involving the use of a heated liquid layer on the surface of the workpiece through which large quantities (at least 90 gph) of ozone diffuse. Claims 26 and 28 describe a processing method involving the use of a heated liquid layer, at about 55 to 120° C, on the surface of the workpiece through which ozone diffuses. The ozone diffuses through the liquid layer and reacts at the surface of the workpiece to remove contaminants or organic materials (such as photoresist) from the surface of the workpiece. See application, page 5, lines 8-16; page 13, line 22 - page 14, line 12; page 17, lines 9-21.
6. Issue: There are two issues on appeal:
 - (a) Whether claims 1-14, 17, 19-21, 23, and 27 are patentable under 35 U.S.C. § 103 over Li et al. (U.S. Patent No. 5,749,975) in combination with Bergman (U.S. Patent No. 5,232,511) or Matsuoka (EP 548,596).

- (b) Whether claims 26 and 28-34 are patentable under 35 U.S.C. § 103 over Li et al. (U.S. Patent No. 5,749,975) in combination with Bergman (U.S. Patent No. 5,232,511) or Matsuoka (EP 548,596), and further in view of Kashiwase et al. (U.S. Patent No. 5,378,317) or Wada et al. (JP 62-117330) or Watarai et al. (JP 04-125927 – “JP ‘927”) or NEC Corp. (JP 05-283389 – “JP ‘389”).

7. Grouping of Claims - Claims 1-14, 17, 19-21, 23, and 27 are in Group I. The remaining appealed claims 26 and 28-30 are in Group II. The claims in Group I are separately patentable from the claims in Group II, for the reasons set forth below in the Argument.

8. Argument

A. Group I Claims

The issues are ripe for appeal as the rejections in the 12/23/02 Office Action have been maintained and have not changed in the 10/29/03 and 4/9/04 Office Actions. Claims 1, 2, and 27 (as well as claim 26) are independent claims that describe improved cleaning methods and systems involving the use of a heated liquid layer on the surface of a workpiece through which large quantities (at least 90 gph) of ozone diffuse. These claims are rejected even though there is no mention of any ozone flow rate whatsoever, anywhere in the prior art. It is well known that adding heat will increase the reaction kinetics of an oxidizer, such as ozone, thereby speeding up process times. However, it is also well known that the solubility of a gas such as ozone, in a liquid, such as water, decreases with increasing temperature (see application, page 5, lines 8-16). This characteristic inverse function of gas solubility versus liquid

temperature suggests the use of liquid or water at room temperature or lower, in order to increase the level of dissolved ozone in the water. Indeed, various prior art techniques using chilled ozonated water have been proposed. While these techniques can achieve high levels of dissolved ozone, reaction times remain low due to the low temperatures. On the other hand, using water at high temperatures has not been effective, due to the decreasing concentration of ozone in the water as temperature increases.

The claimed methods and apparatus achieve the advantages of both high ozone concentration at the workpiece surface, and high temperature, to provide fast reaction times, by using diffusion, rather than dissolution. While only a low amount of ozone can be dissolved within the heated liquid layer on the surface of the workpiece, large amounts of ozone can diffuse through the heated liquid layer to react at the workpiece surface, as claimed.

Page 4 of the 10/29/2003 Office Action (paper 24) asserts that it is obvious to combine references that teach heating a liquid with references that teach treating a workpiece with ozone, as follows:

"This is because using the ozone cause[s] oxide decomposition to occur, and the high[er] the temperature of the ozone cleaning solution, the greater the oxide decomposition effect from the ozone."

While this statement would be reasonable and correct if ozone were highly soluble in hot water or liquid, it is well known that the solubility of ozone in water decreases rapidly with increasing temperature. Consequently, there is no basis for

rejecting the claims over a combination of references that simply teach use of heated liquid and ozone (such as Kashiwase et al, Wada et al, JP '927 or JP '389), because it is not possible to dissolve useful amounts, and certainly not 90 gph, of ozone into the heated liquid.

The "Response to Arguments" section of the 4/9/04 Final Office Action states that "Applicant's argument with respect to the limitation of 'dissolve useful amount of ozone into the heated liquid' is unpersuasive, because the process as claimed does not include this limitation, and the specification, as originally filed, does not provide support for said limitation" (emphasis added). Indeed, the claims do not describe dissolving useful amounts of ozone into a heated liquid, because, as stated throughout the specification, large amounts of ozone cannot effectively be dissolved into a heated liquid (see e.g., application page 14, lines 7-12; page 17, lines 9-16).

Rather, the claims all recite diffusion of ozone through a heated liquid layer, not dissolution of ozone into liquid. As explained above, large amounts of ozone can effectively be diffused through a heated liquid layer. Accordingly, the claimed methods and apparatus are patentably distinct from the cited prior art references, which all teach dissolution.

Claims 1, 2, 26, and 27 all describe introducing ozone at a rate of at least 90 grams per hour (gph), or using an ozone supply system having a capacity of at least 90 gph. This claimed feature is not taught or suggested in any of the cited prior art. Indeed, the 12/23/02 Office Action (paper 13), at paragraph 2, states that "Li et al., Bergman and Matsuoka do not teach the ozone rate as claimed [90 gph]." The other

cited references, which were cited only for the temperature ranges that they disclose, also do not teach the claimed ozone rate.

Li et al., the principle reference, describes a dry cleaning process, and specifically teaches away from employing a wet cleaning process (see cols. 1 and 2), as described in the claims. For example, Li et al. states that, "One of the drawbacks of wet cleaning is that surface tension can prevent the liquid from penetrating into high aspect ratio features, leaving part of the surface uncleaned" (col. 1, lines 49-51). Accordingly, it is improper to combine Li et al. with references that teach wet cleaning processes, such as Bergman and Matsuoka (see MPEP § 2145(X)(D)(2), stating that, "it is improper to combine references where the references teach away from their combination").

Li et al. discloses a surface diffusion layer (col. 4, lines 18-60), which is formed by depositing a vapor on the surface of a wafer (col. 4, line 42). Since Li et al. is a dry-cleaning process, the vapor layer is necessarily extremely thin, with no likelihood of the diffusion layer assisting in maintaining the workpiece at an elevated temperature, as in claim 2. Moreover, in Li et al., the purpose of the diffusion layer is to inhibit direct reaction of the gas phase with the wafer (col. 4, line 33), in order to eliminate surface roughness (col. 2, lines 38-46).

Thus, the intent of Li et al. runs opposite to that of the pending claims. The intent of Li et al. is to inhibit direct reaction of the gas phase with the wafer surface (col. 4, line 33), or, in other words, to decrease the mean free path and create a smooth silicon surface, with less pitting or scoring (col. 4, lines 61-64). Accordingly, Li et al., by implication, encourages using relatively low concentrations of ozone, so that ozone is

less likely to directly react with the wafer surface. In contrast, claims 1, 2, 26, and 27 recite providing an increased amount of ozone to react at the workpiece surface, via diffusion of ozone through a heated liquid layer, which increases the reaction rate. (Ozone may also contact and react at the workpiece surface via entrainment and/or bulk transport.) Because Li et al. teaches inhibiting direct reaction of the gas phase with the wafer surface, it teaches away from using a very high concentration of ozone, and clearly does not suggest providing ozone at the claimed rate of at least 90 gph.

Matsuoka discloses use of ozone and rotation of the workpieces, as noted by the Examiner at paragraph 2 of the 12/23/02 Office Action. However, Matsuoka teaches away from using a heated liquid, as follows:

"A problem with a dry treatment using ozone is that when resists implanted at high doses are treated at relatively high temperatures, pumping, etc., takes place through heat, making some resist residues likely to remain intact." Page 2, lines 56-58.

"Heating the substrates does not permit wet ozone to have well-enough effects, because any thin water film cannot occur even when a wet ozone-containing gas is fed." Page 3, lines 34-35.

Consequently, Matsuoka does not suggest adding ozone at 90 gph, as claimed, since such large quantities of ozone would not dissolve into even the room temperature liquid described therein. Matsuoka, in Example 1, appears to suggest an ozone rate of approximately 25 gph (based on the 6 lpm and 55,000 ppm parameters). There is no

suggestion in Matsuoka to use a higher rate of ozone. The claims, conversely, recite that ozone is provided at a rate of at least 90 gph, i.e., at least a 350% increase over the rate, if any, suggested by Matsuoka. A 350% increase cannot be obvious.

Furthermore, because Matsuoka teaches away from heating, the rate of reaction in Matsuoka is presumably much lower in comparison to the claims, which all recite using a heated liquid. With a lower reaction rate, there would be no motivation to increase the ozone rate in Matsuoka, since there would be no need for additional ozone. Accordingly, there is no suggestion in Matsuoka to introduce ozone at a higher rate, such as the claimed rate of 90 gph.

Bergman teaches uniform etching of a wafer with HF and/or HCl, and makes no mention or suggestion of using high capacity ozone. Thus, Bergman does not teach or suggest introducing ozone into a workpiece-containing environment at the claimed rate of at least 90 grams per hour.

Based on the foregoing, none of the references, alone or in combination, teach or suggest introducing ozone at the claimed rate of at least 90 gph, as recited in claims 1, 2, 26, and 27. Accordingly, a *prima facie* case for obviousness has not been made against these claims (see MPEP §2143.03, stating that "to establish *prima facie* obviousness of a claimed invention, all the claim limitations must be taught or suggested by the prior art"). The claims of Group I are separately patentable from those of Group II because they all describe introducing ozone at a rate of at least 90 grams per hour (gph), or using an ozone supply system having a capacity of at least 90 gph. Except for claim 26, the claims of Group II, as described below, do not include this limitation.

B. Group II Claims

Turning now to the Group II claims, Nos. 26 and 28-34, there are 8 different grounds of rejection, due to the alternative groupings of the principal reference Li, et al., with either Bergman or Matsuoka, and the further combination of either of those two groups, with the four additional tertiary references Kashiwase, et al., Wada, et al., JP'927 and JP'389.

The four tertiary references are cited only for use of temperature ranges from 25°-100°C, 80°-100°C, or temperatures up to 120°C. (10/29/2003 Office Action, para. 6.) The rejections of claims 26 and 28 using these references are entirely flawed here because Li, et al., the principal reference, is silent on any temperature ranges, and that, even more importantly, the prior art itself expressly teaches away from use of such temperature ranges in an ozone process. See the passages from Matsuoka described above (e.g., "Heating the substrates does not permit wet ozone to have well-enough effects..."). In addition, Kashiwase, et al. also teaches against use of heat with ozone, in a non-immersion process:

"In an ozone-processing tank where bubbles of ozone containing gas do not exist, if the processed water is heated to an elevated temperature, the ozone cannot remain dissolved in the processed water since the ozone is immediately decomposed, and thus sufficient effect on an organic film by the ozone cannot be obtained." Kashiwase, et al., column 5, lines 13-19. (emphasis added).

Here, two of the prior art references, Matsuoka and Kashiwase, et al. both expressly teach away from use of a heated liquid in a non-immersion ozone process,

while none of the prior art teaches use of higher temperatures in a non-immersion ozone process.

Turning specifically to each to each the Group II rejections, the principal reference Li , et al. has already been discussed above. However, with respect to claims 26 and 28, Applicant simply points out here that Li , et al.:

- 1.] does not disclose any heating or temperature ranges.
- 2.] does not disclose any controlling thickness of a boundary layer.
- 3.] does not use liquid *per se* in processing, since it is a dry cleaning method.

The secondary reference Bergman is not relevant here because Bergman is cited only in the 12/23/2002 Office Action for the step of rotating. In Bergman, the wafer is rotated to provide uniform dispersion of reactant acid vapors across the wafer surface (Abstract). None of the Group II claims expressly describes rotating.

The other secondary reference Matsuoka, as discussed above, expressly teaches away from heating or elevated temperatures.

Moving on to the four tertiary references, Kashiwase, et al. discloses wet immersion processing, using ozone and heat (Figures 3(b) and 4(b)). In immersion processing, there of course cannot be any liquid layer formed on the workpiece, as claimed, since the workpiece is entirely submerged in a bath of liquid. Kashiwase, et al. also discloses dry single wafer processing in Figures 2 and 4(a). In these embodiments in Kashiwase, et al., the wafer is heated and rotated and exposed to ozone while dry.

Accordingly, in Kashiwase, et al. there is no suggestion of forming a liquid layer on the workpiece, and no mention of diffusion. Kashiwase, et al. discloses temperatures of 40°-100°C (column 4, lines 59), (column 7, lines 65-68). However, these temperatures in Kashiwase, et al. are temperatures of the immersion bath, not temperatures of a liquid layer formed on the workpiece surface, as claimed.

Accordingly, each of the claimed steps of:

- 1.] controlling the thickness of the liquid on the workpiece to form a liquid layer;
- 2.] with the liquid at about 55°-120°C;
- 3.] and with the ozone diffusing through the liquid layer and reacting at the surface of the workpiece;

are not suggested in any one of Li, et al., Bergman and Kashiwase, et al. Perforce, the combination of these references cannot render claims 26 and 28 obvious.

Regarding the combination of Li, et al., Matsuoka, and Kashiwase, et al., Li is totally silent on temperatures. Matsuoka expressly teaches away from heating or temperatures above room temperature. Consequently, there is no motivation to combine them. And indeed there is express motivation in Matsuoka itself not to combine them.

The tertiary reference Wada, et al., JP62-117330 is purely cumulative of Kashiwase, et al. Wada, et al. like Kashiwase, et al., discloses an immersion process, with the liquid bath at 80°-100°C, and with ozone bubbling up through the bath of liquid

(translation, page 2, eighth paragraph). Also like Kashiwase et al., in Wada et al, there is:

- 1.] No suggestion of formation of a liquid layer; and
- 2.] No suggestion of controlling the thickness of the layer, since the concept of a liquid layer on a workpiece is entirely meaningless in immersion processing.

Accordingly, the combination of Li, et al., Bergman and Wada, et al., or the combination of Li, et al., Matsuoka, and Wada, et al., cannot render claims 26 or 28 obvious for the same reasons provided above with respect to the Kashiwase, et al. tertiary reference.

JP '927 describes a purely dry ozone ashing process. The wafer is heated to 120° in an ozone environment. After a certain weight percentage of ozone is consumed, the wafer is sprayed with hot sulfuric acid (translation, page 5, para. 55). Accordingly, there is no wet cleaning. The ozone in JP '927 is used only when the wafer is dry (and at 120°C). As with Kashiwase et al and Wada et al above, JP '927:

- 1.] does not suggest a liquid layer;
- 2.] does not suggest controlling the thickness of a liquid layer, or any form of wet processing or ozone diffusion.

Accordingly, the combinations of Li, et al., Bergman and JP '927, or the combination of Li, et al., Matsuoka and JP '927 cannot render claims 26 or 28 obvious, for the same reasons as described above.

The fourth tertiary reference JP '389 is largely unrelated to claims 26 and 28, and is cumulative to the other tertiary references.

A final consideration is that each of Kashiwase, et al., Wada, et al., JP '927, and JP '389 use acids in the same way as the prior art discussed at pages 1-3 of the Application. On the other hand, the claimed methods require only use of heated liquid and ozone, providing a far more environmentally friendly, economical, and preferred approach.

C. Conclusion

In view of the foregoing, Applicant submits that the claims are not obvious over the cited combination of references. Accordingly, Applicant requests that the Board reverse all of the rejections.

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APPENDIX – Claims in the Appeal

(Claims 15, 16, 18, 22, 24, and 25 have previously been cancelled)

1. A method for processing a workpiece, comprising the steps of:

 providing a liquid at a temperature in the range of about 25-150° C onto a surface of the workpiece;

 introducing ozone into an environment containing the workpiece at a rate of at least 90 grams per hour;

 controlling a thickness of the liquid on the workpiece so as to form a liquid layer that allows for diffusion of the ozone through the layer to the surface of the workpiece; and

 reacting the ozone at the surface of the workpiece, to process the workpiece.

2. A method for cleaning a surface of a workpiece, comprising the steps of:

 providing a heated liquid solution of water and at least one of HF and HCl onto the surface of the workpiece, with the heated solution assisting in maintaining the workpiece at a temperature in the range of about 25-150° C;

 introducing ozone into an environment containing the workpiece at a rate of at least 90 grams per hour;

 controlling a thickness of the heated liquid solution to form a thin liquid boundary layer on the surface of the workpiece to allow diffusion of the ozone

through the boundary layer for reaction at the surface of the workpiece, to clean the workpiece.

3. The method of claim 1 where the ozone is introduced at a rate of at least 130 grams per hour.

4. The method of claim 1 where the ozone is introduced at a flow rate of at least 10 lpm and a concentration of at least 10% by weight.

5. The method of claim 1 wherein the liquid comprises deionized water.

6. The method of claim 5 wherein the deionized water is superheated.

7. The method of claim 1 wherein the liquid includes sulfuric acid, hydrochloric acid, ammonium hydroxide, or deionized water.

8. The method of claim 1 wherein the step of controlling comprises the step of rotating the workpiece.

9. The method of claim 1 wherein the step of controlling comprises the step of rotating the workpiece at a rotation rate equal to or greater than about 300 rpm.

10. The method of claim 1 wherein the step of controlling comprises adding a surfactant to the liquid.

11. The method of claim 1 wherein the step of controlling comprises the step of spraying the liquid onto the surface of the workpiece at a controlled flow rate.

12. The method of claim 1 wherein the liquid includes water and HF at a concentration ratio of between about 50: 1 and 500: 1.

13. The method of claim 1 wherein the liquid includes water and HCl at a concentration ratio of between about 50: 1 and 500: 1.

14. The method of claim 1 wherein the liquid includes water, HF and HCl at a concentration ratio of between about 50: 1: 1 and 500: 1: 1.

17. The system of claim 27 with the ozone supply system comprising a contactor for receiving the ozone and the liquid.

19. The system of claim 27 further comprising a rotor assembly in the chamber for rotating the workpiece.

20. The system of claim 27 where the ozone supply system generates a flow of ozone at a flow rate of at least 10 lpm and a concentration of at least 10% by weight.

21. The system of claim 27 where the heater comprises a steam boiler.

23. The system of claim 27 further comprising means for controlling a thickness of a liquid layer on the workpiece, including at least one of:

a rotor for rotating the workpiece;

a fluid flow controller or one or more nozzles adapted to generate fine droplets of the liquid.

26. A method for processing a workpiece, comprising the steps of:

providing an aqueous liquid boundary layer onto a surface of the workpiece with the liquid boundary layer at a temperature in the range of 55-120° C;

introducing ozone into an environment containing the workpiece at a rate of at least 90 grams per hour;

controlling a thickness of the aqueous liquid boundary layer to allow for diffusion of the ozone through the boundary layer and a reaction at the surface of the workpiece, to process the workpiece.

27. A system for processing a workpiece, comprising:

a process chamber;

means for forming a liquid boundary layer on the workpiece;

an ozone supply system for providing ozone directly or indirectly into the chamber, and having a capacity of at least 90 grams per hour, whereby the ozone can diffuse through the boundary layer to a surface of the workpiece; and

a heater for heating the aqueous liquid to a temperature in the range of 25-150° C before the liquid is provided onto the workpiece.

28. A method for processing a workpiece, comprising the steps of:

providing a liquid at a temperature in the range of about 55-120° C onto the workpiece;

introducing ozone into an environment containing the workpiece;

controlling a thickness of the liquid on the workpiece to form a liquid layer on the workpiece, with ozone diffusing through the liquid layer and reacting at the surface of the workpiece.

29. The method of claim 28 wherein the liquid is at a temperature in the range of 75-115° C.

30. The method of claim 28 wherein the liquid is at a temperature in the range of 85-105° C.

31. The method of claim 1 wherein the liquid is at a temperature in the range of 55-120° C.

32. The method of claim 1 wherein the liquid is heated to a temperature in the range of 75-115° C.

33. The method of claim 27 wherein the liquid is heated to a temperature in the range of 75-115° C.

34. The method of claim 27 wherein the liquid is heated to a temperature in the range of 85-105° C.